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Isotopic and molecular characterization of particulate organic matter in coastal waters.

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Summary

This thesis reports on investigations of the stable and radioactive carbon isotope distributions in sedimentary and suspended particulate organic matter (POM) in coastal waters with the attempt to determine the origin of the POM. POM in coastal waters - estuaries or coastal seas - can have a (i) marine origin, i.e. the ultimate source of the POM is marine phytoplankton, or (ii) a terrestrial origin, as rivers and winds transport POM from the continents to the sea. The rivers alone transport annually more particulate organic carbon to the oceans than the total amount of organic carbon buried in all marine sediments. This means that terrestrial POM is largely mineralized once it enters the sea. In order to understand what is the fate of terrestrial POM in the sea it is necessary to be able to distinguish between terrestrial and marine POM. One method widely used is to analyze the abundance ratio between the two stable isotopes of carbon - ^{13}C and ^{12}C , conventionally expressed as the relative deviation from that of a standard ($\delta^{13}\text{C}$). In general there is a difference between this $\delta^{13}\text{C}$ value in (marine) phytoplankton ($\delta^{13}\text{C}$ around -21‰) and terrestrial plants ($\delta^{13}\text{C}$ around -27‰), due to a phenomenon called isotopic fractionation: the carbon isotopic composition of a POM sample is a measure of fractional contribution of terrestrial and marine organic matter. However, there are some factors that complicate the use of bulk $\delta^{13}\text{C}$ values: 1) $\delta^{13}\text{C}$ values of phytoplankton (and plants) varies, depending on a number of (environmental) factors; 2) different organic compounds in the same organism have different $\delta^{13}\text{C}$ values. Generally, carbohydrates and proteins have higher $\delta^{13}\text{C}$ values than lipids and other cell components. These compounds can degrade at different rates, causing the $\delta^{13}\text{C}$ of the total organic matter mixture to change in time depending on environmental conditions.

This thesis is the result of an extensive study of the ^{14}C abundance as an additional indicator of the origin of POM. The relative ^{14}C abundance (^{14}a), related to the age of organic matter, has been proposed as a possibly useful tracer, because in many rivers POM is mainly derived from erosion of old peat deposits and soils. Because conventionally ^{14}C abundances are corrected for isotopic fractionation (normalized ^{14}a values), the so corrected values are equal for all the components in short living organisms. Therefore, selective degradation, changing the $\delta^{13}\text{C}$, will not affect the ^{14}a of organic matter of a single source.

Apart from ^{14}C as a second indicator of the POM source of the bulk sample, the isotopic analyses were applied to different constituents of total POM, assuming that these fractions are more homogeneous with respect to stability and that, consequently, the $\delta^{13}\text{C}$ value would be much less affected by selective degradation.

To obtain additional information about the nature of the POM the samples were also subjected to pyrolysis-gas chromatography-mass spectrometry.

The first two chapters of this thesis are dealing with the variation in carbon isotopic distributions with particle size in recent sediments from the North-East Pacific off the coast of the state Washington (USA) and from the Ems-Dollard estuary in North-West Europe between the Netherlands and Germany. In the sediment samples from ca. 25 cm deep on the slope and in the so-called Cascadia Basin off the Washington coast, size fractionated by SPLITT-separation, small variations in carbon isotopic compositions are observed, up to 5 ‰ for ^{14}a and 1.3 ‰ for $\delta^{13}\text{C}$. There are no clear trends common to the three samples studied. The bulk samples were also extracted with hot water. For the two deep samples from the Cascadia Basin the $\delta^{13}\text{C}$ values show that the hot water extracts are of marine origin. Their ^{14}C ages, corrected for a reservoir effect of 400 years, are in agreement with the sediment ages obtained by other authors. The bulk samples contain a considerable amount of older material. The hot water extract of the slope sample appeared to be a mixture of organic matter of marine and terrestrial origin, as shown by the $\delta^{13}\text{C}$ value. The terrestrial component is considerably older (ca. 1000 years) than the marine component. Py-GC-MS showed that the organic matter in the three samples is mainly aromatic. Specific markers of lignin were not detected. Specific pyrolysis products of proteins were not found either.

In the surface sediment from the Ems-Dollard estuary a large difference is observed between the ^{14}a of the size fractions finer and coarser than 20 μm . Organic matter in the coarser particles has an average ^{14}a of 52 ‰, contrary to 80 ‰ in the finer particles. Also $\delta^{13}\text{C}$ differs considerably: -23.1 ‰ for the <20 μm fraction and -25.6 ‰ for the >20 μm fraction. Based on these results it appears that the coarse fraction contains a higher amount of organic matter from an old terrestrial source (peat), than the fine fraction. The pyrolysates of the fine fractions contained pyrolysis products of aliphatic macromolecules and compounds derived from proteins and carbohydrates. In the pyrolysates of the coarse fractions the concentrations of the latter compounds were hardly detected.

From the Ems-Dollard estuary also suspended POM was studied. In two sets of samples taken along the salinity gradient, from spring and autumn, the spring samples show an increase in $\delta^{13}\text{C}$ and ^{14}a with increasing salinity. As is shown by comparison with isotope data of the dissolved inorganic carbon (DIC) in the estuarine water and analysis of water extractable organic matter, this is caused mainly by the fact that in the outer estuary primary production is much higher than in the inner part of the estuary. However, some organic matter produced in water with a higher salinity is found in samples from lower salinity water. All samples contain an old fraction as well. In the autumn samples no clear increase in $\delta^{13}\text{C}$ and ^{14}a is observed. In the entire estuary, except at two stations in the middle part, the $\delta^{13}\text{C}$ values are quite similar to that of POM from the Dutch coastal waters of the North Sea (-24 to -23 ‰). The ^{14}a value, however, is considerably lower than that of North Sea POM, showing that it is not identical to North Sea POM. It might be material imported from the North Sea that already spent a relatively long time in the estuary during repeated sedimentation and resuspension. The two samples from the middle part of the estuary have considerably lower $\delta^{13}\text{C}$ and ^{14}a , indicating a large terrestrial component in the POM. The pyrolysates of these samples contain higher concentrations of long chain n-alkanes, indicators of terrestrial matter. Probably an old terrestrial deposit was eroding in the deep tidal channel near the sampling sites.

$\delta^{13}\text{C}$ and ^{14}a of suspended POM vary with season, due to estuarine algal blooms in spring. Not only were the bulk isotopic compositions of a time series of POM samples spanning the years 1992 and 1993 determined, but the samples were also fractionated into a hot water extract, hydrochloric acid hydrolysate, lipid extract, KOH hydrolysate and non-hydrolyzable, insoluble residue. The phytoplankton blooms occurring in spring cause the bulk ^{14}a to increase. The effect on the $\delta^{13}\text{C}$, however, is not always the same. In the two years studied, in one spring season the $\delta^{13}\text{C}$ of the POM increased, while in the other spring season it was the same as during non-bloom periods. As was shown by isotopic analysis of the isolated fractions, this was caused by a difference in the $\delta^{13}\text{C}$ values of the fresh phytoplankton component. The cause of this difference was probably a combination of: a difference in $\delta^{13}\text{C}$ of the carbon source and effects of water temperature, being lower at the time of the spring 1992 sampling, and growth rate, which was lower at the time of sampling in spring 1992, as indicated by the lower organic carbon content. The insoluble, non-hydrolyzable residue of all samples is relatively old material (^{14}a around 40 %), which, based on the $\delta^{13}\text{C}$ values, appears to originate for a considerable part from marine or

estuarine phytoplankton. The main component of POM in the Ems river is peat, that started to be formed in the area around 7000 years ago, which is approximately the same age as for the residues as well. Therefore, old marine organic matter is imported into the estuary or marine organic has a high residence time in the estuary.

Also in the North Sea a seasonal variation in $\delta^{13}\text{C}$ and ^{14}a is observed as well as in organic carbon content of a series of samples of suspended POM spanning the year 1994: high values in spring and summer and lower values in autumn and winter, as in the Ems-Dollard estuary, caused by phytoplankton blooms during these periods. All four samples were fractionated into a hot water extract, hydrochloric acid hydrolysate, lipid extract, KOH hydrolysate and non-hydrolyzable, insoluble residue. The summer sample appeared to be almost homogeneous in ^{14}a , showing that the sample consists almost entirely of fresh phytoplankton. The ^{14}a value of this phytoplankton is remarkably high (120 %), compared to DIC in the ocean (ca. 110 %), to DIC (around 80 %) and POM (85 to 95 %) in the main rivers discharging to this part of the North Sea, and to the atmospheric ^{14}a value (ca. 110 %). The high value might be caused by contamination of North Sea DIC by the nuclear fuel reprocessing plant at La Haye (France). Comparison of the isotope ratios of the winter sample with $\delta^{13}\text{C}$ and ^{14}a values of POM from the rivers Rhine and Meuse show that this sample contains a considerable old component of marine origin. The terrestrial contribution calculated from the $\delta^{13}\text{C}$ values of the individual fractions is lower than resulting from the bulk $\delta^{13}\text{C}$ (40 and 60 % respectively). This can be caused by the selective removal of carbohydrates and proteins, having higher $\delta^{13}\text{C}$ values than other components from the same organism. The winter sample contains, apart from a variety of polar compounds, aliphatic macromolecules, that may have a marine or terrestrial origin. In the summer sample, (almost) entirely consisting of phytoplankton, these macromolecules were not detected. However, the $\delta^{13}\text{C}$ of the insoluble, non-hydrolyzable residue, which contained these macromolecules, indicates that at least part of it is of marine origin.